Atomistic simulation of the structure and elastic properties of pentlandite structure (Ir_9S_8)

M A Mehlape, **D Tanzwani and P E Ngoepe**
Materials Modelling Centre, School of Physical and Mineral Sciences, University of Limpopo, South Africa, Private Bag, X1106, SOVENGA, 0727

Email:mofuti.mehlape@ul.ac.za

Abstract. Atomistic simulation was carried out to study the effect of pressure on the structureand elastic properties of pentlandite structure (Ir_9S_8) sulphides. The lattice parameters, bond lengths and elastic constants as a function of pressure are calculated. Pentlandite is a major precious metals-bearing mineral and plays a very important role in mining. Precious metal ores co-exists with base metals either as solid-solution and intergrowths, hence rendering its detailed understanding important for efficient extraction of these precious metals. This work relates to problems in applied areas such as mineralogy, geophysics and geochemistry, whereby phase transition is modified by impurities, so there is the additional concern of the effect of high pressures. We want to see how pressure changes the lattice parameters, elastic constants and bond lengths. We used computational techniques to investigate the effect of high pressure on the pentlandite structure. It was noted that as the pressure increases, the volume decreases. The elastic properties were found to be positive, which satisfies the conditions for a mechanically stable cubic structure.

1. Introduction

The Bushveld Complex has the largest concentration of platinum group elements (PGEs) and these are ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt) [1]. Pentlandite minerals are known to host such precious metals, either as solid solutions or as intergrowths [2] and in order to achieve high recoveries of such metals it is necessary to float pentlandites efficiently, particularly in reefs that are less explored, such as the platreef. These PGEs exist in different structures and they could form pentlandite structure (Ir_9S_8), which makes them significant sulphide minerals. Owing to their high concentration in the Bushveld Complex, it draws much attention in investigating their structure and elastic properties. In one of the studies of sulphide minerals within the Merensky Reef deposit of the Bushveld Complex, it was found that Ir, Os and Ru reside in solid solution in pentlandite and pyrrhotite, Rh and some Pd in pentlandite [3]. Our focus is on the atomistic simulation of structural and elastic properties of iridium-bearing mineral within pentlandite (Ir_9S_8). Ir has properties that are resistant to corrosion, and together with its alloys is used in chemical industry, medical devices and jewellery manufacture [4]. The study on the elastic properties of minerals play key role in the studies of earth's deep interior [5]. Furthermore, theory and computation play an increasingly important role in the field of mineral physics by allowing the scientist to probe environments, such as the deep Earth, that are challenging or impossible to access extensively by experiment [6]. Determination of high-pressure mineral structure is crucial for understanding all other pressure-induced property changes in the deep Earth [7]. Elastic properties describe the volume and shape changes that occur when stresses are applied to a material [8].

Pentlandite, Ir_9S_8 structure

The conventional unit cell of the pentlandite has the formula $Ir_{36}S_{32}$ and contains a cubic close-packed arrangement of sulphide ions containing 64 tetrahedral holes and 32 octahedral holes. Of the 64 tetrahedral holes, 32 are occupied by Ir^{2+} ions, these being distributed through the lattice in groups of eight which lie at the corners of sub-cubes of edge length 0.250 nm. Of the 32 octahedral holes, 28 are pseudo-octahedral, distorted, and empty, whereas four are truly octahedral and each contains an Ir atom in a formally zero oxidation state. Thus the solid attains the overall stoichiometry Ir_9S_8 [9]. Figure 1 shows the conventional unit cell of Ir_9S_8. The Ir_9S_8 has a space group *Fm3m*.

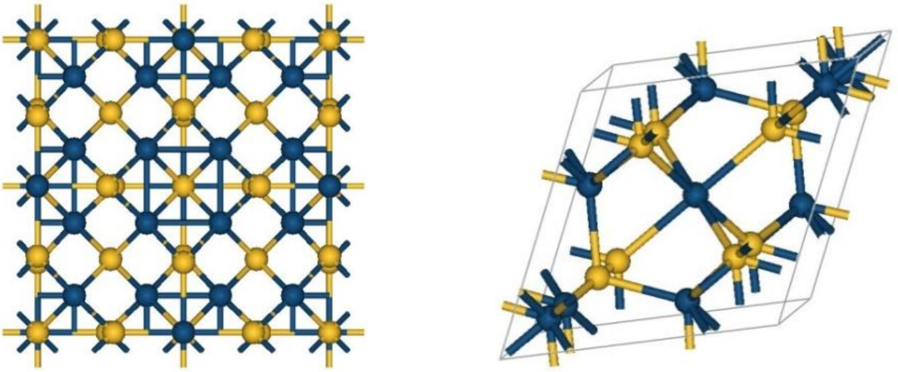

Figure 1: Conventional ($Ir_{36}S_{32}$) and primitive (Ir_9S_8) unit cell of pentlandite structure. Blue and yellow spheres represent metal (Ir) and sulphur (S) atoms respectively.

2. Computational Method

The atomistic simulation method uses interatomic potential functions to describe the total energy of a system in terms of atomic coordinates [10]. The atomistic simulation method in this study was conducted using General Utility Lattice Program (GULP) code [11], which requires the use of interatomic potential functions. GULP code allows the use of two-body, three-body, four-body, six-body, and many body potentials depending on demands of research [12]. The cell geometry of Ir_9S_8 was assigned as a = b = c = 9.928 Å, and $\alpha = \beta = \gamma = 90$ with space group *Fm3m*. Geometry optimization calculations were performed on the structure and elastic constants at pressures ranging between 0 and 40 GPa in the steps of 5 GPa. In this work, we consider the approximation for describing the pentlandite structure, which is the rigid ion model potential. This is an empirical approach and relies on a set of parameters, which were modified using cobalt pentlandite potentials (Co_9S_8) [13]. The potential models can accurately describe the bulk and surface structure properties, lattice constants, and elastic properties of sulphides [14], oxides [15], and other pentlandite structures [16]. The calculations are based on the Born ionic model [17] of a solid and parameters were derived for short range interactions represented by the Buckingham potential, Morse potential and three body terms:

Buckingham Potential

In the Buckingham potential, the repulsive term is replaced by an exponential term and potential takes the form

$$U(r_{ij}) = A_{ij}exp(-r_{ij}/\rho_{ij}) - C_{ij}r_{ij}^{-6} \tag{1}$$

where $A_{ij}$and ρ_{ij} are parameters that represent the ion size and hardness, respectively, while C_{ij} describe the attractive interaction and r_{ij} is the distance between ion i and ion j. The first term is known as the Born-Mayer potential and the attraction term (second term) was later added to form the Buckingham potential. Very often, for the cation-anion interactions, the attractive term is ignored due to the very small contribution of this term to the short-range potential, or, alternatively, the interaction is subsumed into the A and ρ parameters.

Morse Potential

The Morse potential is used to model the interactions between covalently bonded atoms and has the form

$$U(r_{ij}) = D_{ij}\left(\left(1 - exp\left(-\beta_{ij}(r_{ij} - r_0)\right)\right)^2 - 1\right) \qquad (2)$$

where D_{ij} is the bond dissociation energy, r_0 is the equilibrium bond distance, and β_{ij} is a function of the slope of the potential energy well. The Coulombic interactions between covalently bonded atoms are often partially or totally ignored as the Morse potential already contains the attractive component of the interaction between neighbours.

Three-Body Potential

A further component of the interactions of covalent species is the bond-bending term, which is added to take into account the energy penalty for deviations from the equilibrium value. Hence, this potential describes the directionality of the bonds and has a simple harmonic form:

$$U(\theta_{ijk}) = \frac{1}{2}k_{ijk}(\theta_{ijk} - \theta_0)^2 \qquad (3)$$

where k_{ijk} is the three-body force constant, θ_0 is equilibrium angle and θ_{ijk} is the angle between two interatomic vectors $i - j$ and $j - k$. Table 1 gives the potential parameters used in this study.

Table 1: The modified potential parameters for pentlandite structure (Ir_9S_8) used in this study.

Potential			
Buckingham potential	$A_{ij}\,(eV)$	$\rho_{ij}\,(\text{Å})$	$C_{ij}\,(eV\text{Å}^6)$
S-S	1130.533064	0.184528	0.00
Morse potential	$D_{ij}\,(eV)$	$B_{ij}\,(eV)$	$r_0\,(\text{Å})$
Ir-S	3.0	1.633754	2.20
Three body potential	$k_{ijk}\,(eV.rad^{-2})$	$\theta_0\,(°)$	
S-Ir-Ir	0.82	109.503	
Ir-S-S	2.89	109.503	
Ion charges		Charge (e)	
Metal (Ir) core		0.40	
Sulphur (S) core		-0.45	

3. Results and Discussions

The effect of pressure on the structural and elastic properties of pentlandite is discussed in this section. First we discuss the structure and elastic properties under zero pressure. Table 2 shows that optimized structural parameters are in good agreement with the experimental and other theoretical results. A pentlandite cubic structure M_9S_8 has three independent elastic constants (C_{11}, C_{12} and C_{44}). The elastic constants of a typical cubic structure obey the criteria $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. As a result calculated values of elastic constants satisfy both the structural and cubic stability conditions, meaning that the crystal structure is stable under zero pressure.

Table 2 Comparing our results with previous experimental and theoretical data for pentlandite under zero pressure. [a] [18], [b] [19], [c] [20], [d] [21], [e] [22].

Parameter	Present Study	Other Theoretical	Experimental
Lattice parameters			
$a(\text{Å})$	9.809	9.948[a], 9.918[b], 9.927[c], 9.977[d]	9.928[e]
$V(\text{Å}^3)$	943.86	974.44[b]	978.56[c]
Bond lengths (Å)			
Ir-S	2.111	2.122[c]	2.127[d]
Ir-Ir	2.468	2.514[c]	2.505[d]
Elastic Constants (GPa)			
C_{11}	209.5	212.0	
C_{12}	121.1	123.8	
C_{44}	49.9	49.4	
Bulk Modulus (GPa)	150.5	153.2	

Pressure effect

We determine the structure and elastic constants of pentlandite structure up to the pressure of 40 GPa. The effect of high pressure on the structure and elastic properties of pentlandite are reported to further validate the modified potential model. It was reported that, the effect of pressure on the elastic properties in materials is important for predicting and understanding some physical properties like, the interatomic forces, mechanical stability, phase transition mechanisms, dynamic fracture, earthquakes and the internal structures of earth [12]. Again the behavior of earth materials at high pressure is central to our understanding of the structure, dynamics, and origin of the earth [23]

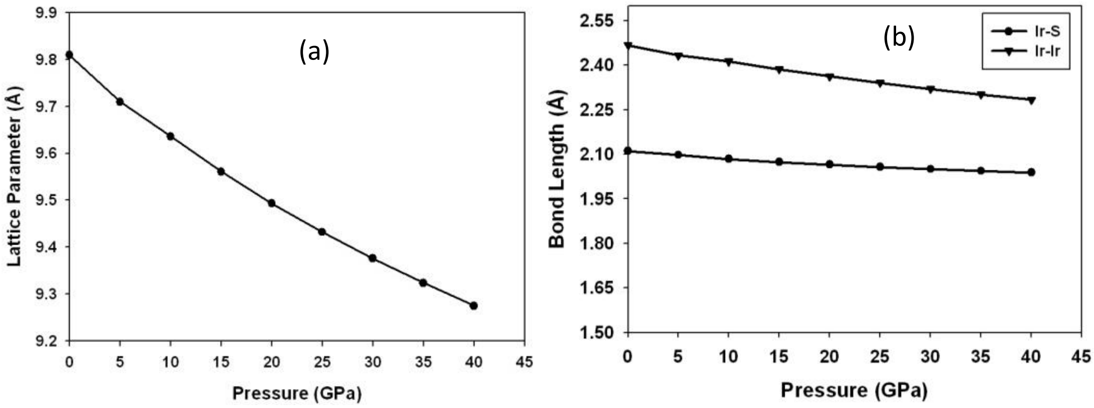

Figure 2: The (a) lattice parameter and the (b) bond lengths as a function of increasing pressure.

.

Figure 2 (a) shows the graph of lattice parameter as a function of increasing pressure. As expected the lattice parameter decreases with the increasing pressure ranging between 0 and 40 GPa. Figure 2(b) shows the graph of bond lengths as a function of pressure. In both cases the actual change is linear with increasing pressure; however bond lengths for Ir-Ir are predicted to shorten much more slowly than those of Ir-S pair, due to the metallic behaviour of pentlandite structure.

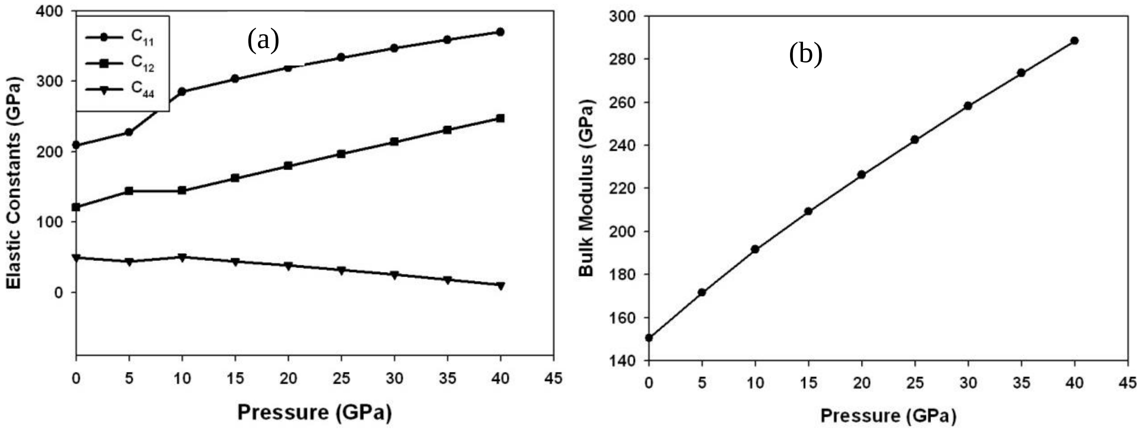

Figure 3: The variation of the (a) elastic constants and (b) Bulk modulus as a function of increasing pressure.

Figure 3(a) represents the elastic constants (C_{11}, C_{12} and C_{44}) of M_9S_8 at the pressure interval between 0 GPa and 40 GPa. The elastic constants C_{11} and C_{12} show a positive and smooth increase as a function of increasing pressure; however C_{44} show a decrement as a function of increasing pressure. Similar observations of the decrement of C_{44} with the increasing pressure have earlier been reported by Varshney et al [23] for the strontium chalcogenides. This implies that $C_{11}$and C_{12} are more sensitive to the change of pressure than the C_{44}. It has been reported by Karki and coworkers [24] that elastic constants increase monotonically with increasing pressure; and that in few cases whereby elastic constants decrease with increasing pressure which implies an elastic instability. There are no available experimental and theoretical data to cross-check the present results, however these results can provide a useful reference for future studies. The variations in bulk modulus with increasing pressure are shown in Figure 3(b). It can be seen from the graph that bulk modulus increase as pressure increases, which shows that the hardness of these material increases with increasing pressure. The increment is expected due to its direct proportionality to applied pressure ranging between 0 GPa and 40 GPa.

4. Conclusion

Atomistic simulation has been carried out to study the effect of pressure on structure and elastic properties of pentlandite structure, Ir_9S_8. The structural properties suggest good agreement when compared with experimental and other theoretical data. The elastic constants were found to be positive, which satisfies the conditions for a mechanically stable cubic structure. Thus the refitted potentials gave reasonable results and may further be helpful to future studies regarding the structural and elastic properties, and other related properties of pentlandite structure.

Acknowledgements

The work was done at the Materials Modelling Centre (MMC), University of Limpopo. The authors acknowledge the National Research Foundation (NRF) for their financial support.

References

[1] O'Connor T C and Shacklenton N J 2013 *Platin. Met. Rev.* **57** 302
[2] Wang Q and Heiskanen K 1990 *Int. J. Miner. Process.* **29** 99
[3] Ballahaus C and Sylvester P 2000 *J. Petrol.* **41** 545
[4] Vidhate K 2015 *Adv. Appl. Sci. Res.* **6** 180
[5] Bass J 2008 *Phys. Earth Planet. Inter.* **170** 207
[6] Gale J D and Wright K 2010 *Rev. Mineral. Geochem.* **71** 391
[7] Yuan H and Zhang L 2017 *Matter. Radiat. Extreme*. **2** 117
[8] Bass J D, Sinogeikin S V and Li B 2008 *Elements* **4** 165
[9] Hoodless R C, Moyes R B and Wells P B 2006 *Catal. Today* **114** 377

[10] Liu Z-J, Sun X-W, Song T, Guo Y, Zhang C-R and Zhang Z-R 2016 *Bull. Mater. Sci.* **39** 1319
[11] Gale J D 1997 *J. Chem. Soc.:Faraday Trans.* **93** 629
[12] Güler E and Güler M 2013 *Adv. Mater. Sci. Eng.* Article ID 525673, 5 pages.
[13] Mehlape M A 2013 *PhD Thesis*. University of Limpopo
[14] Sithole H M, Ngoepe P E and Wright K 2003 *Phys. Chem. Miner.* **30** 615
[15] Maphanga R R, Ngoepe P E and Parker S C 2009 *Surf. Sci.* **603** 3184
[16] Mehlape MA, Ngoepe P E and Parker S C 2013 Proceedings of SAIP 98-103 Available online at http://events.saip.org.za
[17] Born M and Huang K. 1954 *Dynamical Theory of Crystal Lattices 1st edition*. Oxford: University Press
[18] Sidik R A and Anderson A B 2006 *J. Phys. Chem. B* **110** 936
[19] Chauke H R, Nguyen-Manh D, Ngoepe P E, Pettifor D G and Fries S G 2002 *Phys. Rev. B* **66** 155105
[20] Burdett J K and Miller G J 1987 *J. Am. Chem. Soc.* **109** 4081
[21] Rajamani V and Prewitt C J 1975 *Can. Mineral.* **13**, 75
[22] Lindqvist M, Lundqvist D and Westergren A 1936 *Svensk Kem. Tidskr.* **48** 156
[23] Varshney D, Jain S, Shriya S and Khenata R 2016 *J. Theor. Appl. Phys.* **10** 163
[24] Karki B B, Stixrude L and Wentzcovitch R M 2001 *Rev. Geophys.* **39** 507